

PTO 09-1901

CC=JP DATE=20021218 KIND=A
PN=2002363675

BIOCOMPATIBLE Co-BASED ALLOY AND METHOD FOR PRODUCING THE SAME
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UNITED STATES PATENT AND TRADEMARK OFFICE
Washington, D.C. January 2009

Translated by: FLS, Inc.

PUBLICATION COUNTRY	(19) : JP
DOCUMENT NUMBER	(11) : 2002363675
DOCUMENT KIND	(12) : A
	(13) : PUBLISHED UNEXAMINED APPLICATION (Kokai)
PUBLICATION DATE	(43) : 20021218
PUBLICATION DATE	(45) :
APPLICATION NUMBER	(21) : 2001172377
APPLICATION DATE	(22) : 20010607
INTERNATIONAL CLASSIFICATION	(51) : C22C 19/07; A61L 27/00; C22F 1/10; C22F 1/00
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APPLICANT	(71) : JAPAN SCIENCE AND TECHNOLOGY AGENCY
TITLE	(54) : BIOCOMPATIBLE Co-BASED ALLOY AND METHOD FOR MANUFACTURING THE SAME
FOREIGN TITLE	[54A] : SEITAIYO CO KI GOKIN OYOBI SONO SEIZO HOHO

[Claims]

/2*

[Claim 1] A biocompatible Co-based alloy having a composition comprising Cr (from 26 to 30 % by mass), Mo (from 6 to 12 % by mass), and C (from 0 to 0.3 % by mass), the balance being essentially Co, and having a structure in which a granular second phase is finely dispersed in a matrix consisting of crystal grains having an average crystal-grain size of 50 µm or smaller.

[Claim 2] A method for producing a biocompatible Co-based alloy comprising: quench-casting a Co-based alloy having the composition described in Claim 1 with a water-chilled copper mold and forging the obtained ingot at from 1000 to 1300 °C, thereby adjusting the structure to a structure in which a granular second phase is finely dispersed in a matrix consisting of crystal grains having an average crystal-grain size of 50 µm or smaller.

[Detailed Description of the Invention]

[0001]

[Field of Industrial Application] The present invention pertains to a biocompatible Co-based alloy that has excellent corrosion resistance, wear resistance, and processability and, as such, renders itself ideal as a prosthetic bone material, and it also pertains to its production method.

[0002]

* Claim and paragraph numbers correspond to those in the foreign text.

[Related Art] As heretofore known biocompatible alloys, there are Co-Cr cast (HS-21) or wrought (HS-25) Vitallium, Co-Ni-Cr-Mo alloy (MP35N), and so forth, but Vitallium is predominantly used owing to a large number of its clinical data and past uses and its high stability. Vitallium was developed as a dental alloy, and, with later improvements, its application has expanded to the orthopedic field. Besides this, this type of alloy is also available on the market under many trade names, including Alivium, Endcast, Orthochrome, Orthochrome plus, Protasul, and Zimaloy. Vitallium was put to practical use 10 years later than stainless steel, in 1937, but, owing to its corrosion resistance superior to that of stainless steel and also having both sufficient strength and toughness, it is used as artificial hip joint prosthetic materials, such as a bone head, stem, and so forth.

[0003] Cast Vitallium (HS-21) is a high Cr (30 % by mass)-Co alloy containing from 5 to 7 % by mass Mo, and, among the different kinds of Vitallium, it has the best corrosion resistance and hardly has problems of pitting corrosion, crevice corrosion, intergranular corrosion, stress corrosion cracking, and the like in practical use. However, it is susceptible to having internal defects, such as shrinkage holes, bubbles, segregation, and so forth, and has a shortcoming of low fatigue strength (250 MPa). Wrought Vitallium (HS-25) contains W in place of Mo and is an alloy that was improved by replacing a part of Cr with Ni to eliminate shrinkage holes, segregation, and the like, which are the shortcomings of the cast

material. Wrought Vitallium (HS-25) acquires malleability/ductility that are superior to those of annealed stainless steel by a solution treatment and strength comparable to that of wrought stainless steel by cold working. Its corrosion resistance is better than that of stainless steel but is not satisfactory for long-term implant use; therefore, it is used as bone plates, wires, and the like for short-term anchoring use.

[0004]

[Problems that the Invention Intends to Solve] Increasing the Mo content of wrought Vitallium improves its corrosion resistance and wear resistance. In fact, high Mo-Vitallium, in which Mo is increased to 10 % by mass, is known to exhibit corrosion resistance and wear resistance superior to those of the alloy of the original composition. However, because the plasticity processability of Vitallium decreases along with the increase of Mo content, it is difficult to control the microstructure of high Mo-Vitallium by plastic working.

[0005] For cast Vitallium, elimination of its internal defects by adjusting heat history has been investigated. Generally speaking, the shrinkage holes and bubbles formed in a cast alloy are crushed and the dendrite structure is also destroyed by forging, and a uniform structure is created by subsequent recrystallization annealing. For Vitallium, however, there are numerical data pertaining to improvements of its mechanical properties, but not enough knowledge has been obtained pertaining to the relationship between heat history

and the structure and to changes in the mechanical properties resulting from it. As a consequence, in spite of being a material having the advantages of both the stainless steel system, which has excellent processability, and titanium-based alloys, which have excellent strength, corrosion resistance, and the like, Vitallium has low demand, only 20 % or thereabouts of the whole demand, and has not achieved extensive practical use.

[0006]

[Means for Solving the Problems] The present invention was devised to solve these problems, and it intends to provide a biocompatible Co-based alloy having high corrosion resistance and high wear resistance by increasing the Mo content and also by adjusting the structure by means of plastic working.

[0007] The biocompatible Co-based alloy of the present invention, for achieving its objectives, is characterized by having a composition comprising Cr (from 26 to 30 % by mass), Mo (from 6 to 12 % by mass), and C (from 0 to 0.3 % by mass), the balance being essentially Co, and by having a structure in which a granular second phase is finely dispersed in a matrix consisting of crystal grains having an average crystal-grain size of 50 μm or smaller.

[0008] This Co-based alloy is produced by quench-casting a Co-based alloy having a prescribed composition, using a water-chilled copper mold, and by forging the obtained ingot at from 1000 to 1300 °C.

[0009]

[Operation] The present invention improves the corrosion resistance and wear resistance of Vitallium by increasing its Mo content and by adjusting its structure. The effect of Mo on the corrosion resistance and wear resistance becomes pronounced when the Mo content is 6 % by mass or more but reaches its limit at 12 % by mass, and containing Mo in an amount exceeding this adversely affects plasticity processability. Cr is required in a quantity of 26 % by mass or more for achieving corrosion resistance, but an excess quantity exceeding 30 % by mass adversely affects the plasticity processability. The content of C, which is added as necessary, is controlled to 0.3 % by mass or less from the standpoint of wear resistance and plasticity processability.

[0010] For the structural adjustment, quench-casting is carried out using a water-chilled copper mold so as to inhibit the growth of deposits, and plastic working, such as hot forging or the like, is implemented to finely disperse the second phase, such as deposits, intermetallic compounds, and the like. The influence of quenching in the casting process on the growth inhibition of deposits becomes pronounced when the cooling from the pouring temperature down to 400 °C is carried out at a cooling rate of 1000 °C/minute or faster. Hot forging destroys the cast structure, such as dendrite or the like, and forms a matrix composed of isometric crystal grains that are made finer to a size of 50 μm or smaller. Making the matrix finer is also effective for improving wear resistance. However, simply increasing

the Mo content to 6 % by mass or more causes the loss of plasticity processability for forging or the like, and, consequently, a forged high Mo-Vitallium alloy cannot be produced.

[0011] High Mo-Vitallium containing 6 % by mass or more Mo generates a brittle intermetallic compound phase (σ phase) at a temperature from 700 °C or thereabouts to the lower temperature side. Accordingly, in the present invention, by selecting the heat treatment method and processing temperature, the formation of the σ phase is inhibited. More specifically, for the system of the present invention in which the Mo content is set to from 6 to 12 % by mass, the hot forging temperature is set in a range of from 1100 to 1400 °C. By employing quenching, such as water chilling or the like, for cooling high Mo-Vitallium that has undergone hot forging down to room temperature, the formation of the σ phase is prevented, and, instead of the growth of the second phase, granular deposits or crystallized products are finely dispersed in the matrix.

[0012]

[Working Example 1] Co-based alloys (600 g) having the compositions shown in Table 1 were melted with a high-frequency vacuum melting furnace, and the 15500 [sic] °C liquid metals were poured into water-chilled copper molds and subjected to quench casting at a cooling rate (2300 °C/minute) that could bring the temperature down to 400 °C or lower in 30 seconds. Fig. 1 shows the tensile characteristic of each as-cast material at room temperature. The Co-Cr-Mo ternary

alloys showed improved elongation as the addition quantity of Mo increased. Nos. 4 and 5, to which Ni was added, exhibited high elongation/ductility.

[0013]

TABLE 1: VARIOUS Co-BASED ALLOYS USED IN WORKING EXAMPLE

試料 No. (a)	合金成分及び含有量 (質量%) (b)				
	Cr	Mo	Ni	C	Co
1	29	6	—	0.02	残部 (c)
2	29	8	—	0.02	残部 (c)
3	20	10	—	0.02	残部 (c)
4	20	10	16	0.02	残部 (c)
5	20	10	24	0.02	残部 (c)

Key: a) sample No.; b) alloy constituents and contained quantities (% by mass); c) balance

[0014] Using Sample No. 1 alloy, which showed the lowest elongation/ductility in the as-cast state, the influence of a heat treatment on elongation/ductility was investigated, and the results are shown in Fig. 2. For comparison, the influence of a heat treatment on the elongation/ductility of the same Sample No. 1 whose structure was adjusted by 1100 °C hot forging is also shown in the same figure. As is evident from Fig. 2, the quenching effect worked on the as-cast material that was not forged, and the as-cast material and quenched material (aging for 2 hours at 1050 °C, followed by water quenching) both exhibited low elongation/ductility. Especially the furnace-cooled material, which was cooled in the furnace after the 1050 °C aging

treatment, exhibited extremely lower elongation/ductility.

Elongation/ductility was dramatically improved by hot forging.

[0015] In order to investigate the reason for the difference in elongation/ductility between the as-cast material and furnace-cooled material, the metal structure of each material was examined with an optical microscope. The as-cast material (Fig. 3) had a metal structure in which a Mo-rich b.c.c. phase deposited in a granular form, but, in the furnace-cooled material (Fig. 4), a σ phase had grown in a linear shape. Since the σ phase is a brittle deposit that works as the origin of fracture, it is conjectured to be the cause for the low elongation/ductility in the tensile test. With the hot-forged material, which exhibited high elongation/ductility, no linear σ phase was detected, and the material had a structure in which a granular b.c.c. phase was finely dispersed.

[0016] From the relationship between elongation/ductility and metal structures, it can be seen that the increased Mo content is not the direct cause that impairs the high-temperature malleability of Co-Cr-Mo ternary alloys and that, if hot forging is conducted by setting the forging temperature to 1000 °C or higher (preferably 1100 °C or higher), under which condition the deposition of the σ phase can be inhibited, a Co-based alloy having excellent elongation/ductility can be obtained. The material to be forged is preferably one that is quench-cast with the use of a water-chilled copper mold so as to inhibit the deposition of the σ phase. From the above results, it was

confirmed that, by controlling the casting conditions and forging conditions, Co-Cr-Mo ternary alloys having excellent elongation/ductility, in other words, processability, can be obtained. Hence, the Co-Cr-Mo ternary alloys shown in Table 2 were melted and used to investigate the influences of quench casting and hot forging.

[0017]

TABLE 2: Co-BASED ALLOYS USED HEREIN

合金 No. (a)	合金成分及び含有量 (質量%)(b)					備 考 (c)
	Cr	Mo	Ni	C	Co	
1	19	10	91	0.02	残部	MP35N相当(d)
2	29	6	—	0.02	残部	標準的な Vitallium 相当(e)
3	29	9	—	0.02	残部	高 Mo-Vitallium 相当(f)
4	29	12	—	0.02	残部	高 Mo-Vitallium 相当(f)

Key: a) alloy No.; b) alloy constituents and contained quantities (% by mass); c) comment; d) equivalent to MP35N; e) equivalent to standard Vitallium; f) equivalent to high Mo-Vitallium

[0018] Alloys No. 1 and 2 were quench-cast at a cooling rate that could bring down the temperature to 400 °C or lower in 30 seconds after the pouring, and the obtained ingots were subsequently heated to 1100 °C and subjected to hot forging. When the metal structure was examined after the forging, both alloys were found to have an isometric crystal structure (Figs. 5 and 6). Alloy No. 1 had an average crystal-grain size of approximately 100 μm, and alloy No. 2 had an average crystal-grain size of approximately 50 μm. The result of the structural observation of alloy No. 2 revealed the deposition or crystallization of the second phase along the grain boundary, which was not found in alloy No. 1. The deposits or crystallized products

are believed to be a Mo-enriched phase having a b.c.c. crystal structure, judging from the calculated state diagram obtained by Thermo-Calc software and the result of EDS analysis. Alloys No. 3 and 4 were thermally treated at 1100 °C for 4 hours, without forging the ingots. The examination of their metal structures after the heat treatment revealed that both had a dendrite-form solidification structure (Figs. 7 and 8).

[0019] The surface of a test piece that was cut from each alloy No. 1 through 4 was given final polish finishing with a No. 4000 lapping film, and the test piece was subsequently used for an abrasion test. For the abrasion test, a pin-on-flat reciprocating abrasion tester that used an alumina ball was employed, and the test conditions employed were: atmospheric ambience, 10 mm amplitude, 200000 mm sliding distance, and 8.33 Hz sliding speed. As seen from the test results shown in Fig. 9, compared with alloy No. 1, which was equivalent to MP35N, alloys No. 2 through 4, which were equivalent to Vitallium, had far superior wear resistance. From this, it can be said that the addition of Ni to a Co-Cr-Mo ternary composition at a high concentration is effective for improving elongation/ductility but is not advantageous for achieving high wear resistance.

[0020] The wear volumes of Vitallium-equivalent alloys No. 2 through 4 were further investigated in detail, and the obtained results are shown in Fig. 10. Since alloy No. 4 kept the solidification structure containing the largest amount of Mo, its wear

volume was the smallest. On the other hand, alloy No. 2 was a material whose Mo content was the smallest, but its wear volume was found to be approximately the same as that of alloy No. 4. The good wear resistance of alloy No. 2 was the result of adjusting its microstructure by hot forging. That is to say, wear resistance is improved by increasing the Mo content, but it can be further improved by making the structure finer. Next, by hot forging Co-Cr-Mo ternary alloys while varying the forging conditions, such as the forging temperature, rolling reduction, and so forth, the crystal grain size of the forged material was varied, and the effect of the crystal grain size on wear volume was investigated. As seen from the investigation results shown in Fig. 11, wear resistance was improved as the crystal grains became smaller, and the wear volume decreased dramatically at a crystal grain size of 15 μm or smaller.

[0021]

[Working Example 2] Six hundred grams of a Co-based alloy having the composition of alloy No. 3 in Table 2 was melted in a high-frequency vacuum melting furnace, and the obtained 1550 °C liquid metal was poured into a water-chilled copper mold and quench-cast at the same cooling rate as the one used in Working Example 1. The obtained ingot was clad with a hollow rod made of SUS 316L stainless steel and hot forged at from 1100 to 1400 °C, thereby adjusting the structure. By cladding the ingot with stainless steel, direct contact between the forging tool and ingot was prevented, and the ingot could

be kept at a high temperature of 1100 °C or higher during the forging. As a consequence, the deposition of the σ phase during the hot forging could be prevented. Until the thickness, including that of the cladding material, became 20 mm, a cycle of hot forging - 1250 °C annealing was repeated, and, at the end, after 1250 °C x 2 hour annealing, water quenching was performed.

[0022] Thereafter, the forged material was cold-rolled, thereby obtaining a cold-rolled material having a thickness of 5 mm. By immersing the cold-rolled material in an acid mixture of concentrated hydrochloric acid: concentrated nitric acid = 3: 1 (volume ratio), the stainless steel on the surface of the cold-rolled material was eliminated by etching. The material was further annealed at 1250 °C for 1 hour and quenched with water, after which it was subjected another cold rolling, thereby obtaining a 50 μ m-thick sheet material. From this production performance, it can be seen that the Co-based alloy of the present invention, making use of its excellent processability, can be formed into shapes that are suitable for various kinds of artificial bone materials.

[0023]

[Effects of the Invention] As explained in the foregoing, in the biocompatible Co-based alloy of the present invention, the Mo content is set to a larger volume, from 6 to 12 % by mass, and, at the same time, its crystal structure is made finer by quench casting that can finely disperse the second phase and by hot forging that can inhibit

the formation of the σ phase. As a consequence, the alloy of the present invention can be used as a biocompatible material that has further improved wear resistance and that makes use of the excellent characteristics that Vitallium originally has.

[Brief Explanation of the Drawings]

[Fig. 1] A graph that shows the strain-stress curves of various types of Co-based alloys.

[Fig. 2] A graph that shows the influence of the production conditions on the strain-stress curve of a Co-based alloy.

[Fig. 3] A photograph showing the metal structure of an as-cast Co-based alloy material.

[Fig. 4] A photograph showing the metal structure of a furnace-cooled Co-based alloy material.

[Fig. 5] A photograph showing the metal structure of alloy No. 1 used in the working example that was hot-forged.

[Fig. 6] A photograph showing the metal structure of alloy No. 2 used in the working example that was hot-forged.

[Fig. 7] A photograph showing the metal structure of alloy No. 3 used in the working example that was thermally treated.

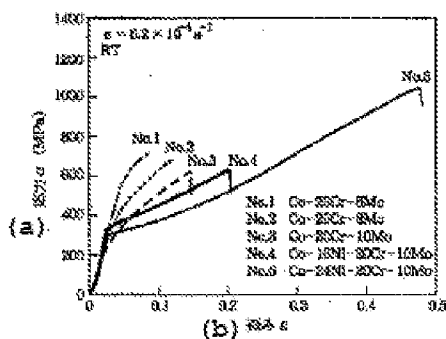
[Fig. 8] A photograph showing the metal structure of alloy No. 4 used in the working example that was thermally treated.

[Fig. 9] A graph that shows the wear characteristic of various types of Co-based alloys.

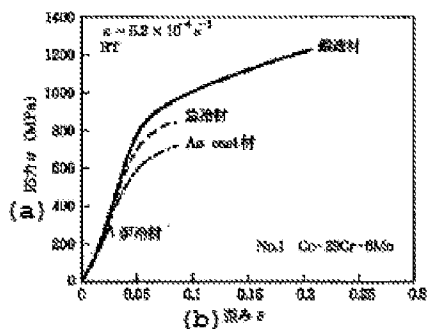
[Fig. 10] A graph that shows the wear characteristic of various types of Co-based alloys.

[Fig. 11] A graph that shows the influence of crystal-grain size on the wear resistance of a forged Co-based alloy material.

[FIG 1]



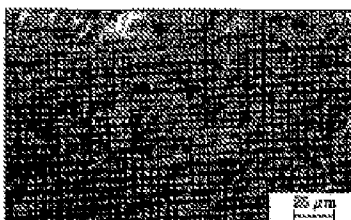
[FIG. 2]



Key: a) stress; b) strain

[FIG. 3]

AS-CAST SAMPLE NO. 1 MATERIAL



[FIG. 4]

FURNACE-COOLED SAMPLE NO. 1 MATERIAL



Key: σ) σ phase

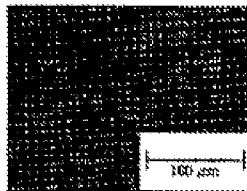
[FIG. 5]

HOT-FORGED ALLOY NO. 1 MATERIAL



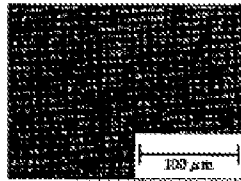
[FIG. 6]

HOT-FORGED ALLOY NO. 2 MATERIAL



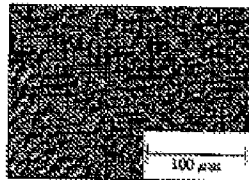
[FIG. 7]

HEAT-TREATED ALLOY NO. 3 MATERIAL



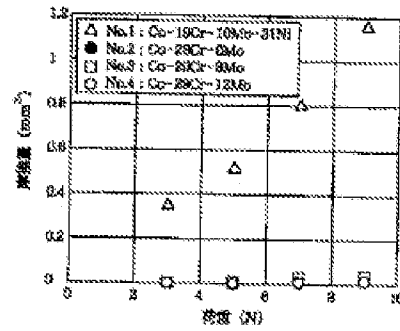
[FIG. 8]

HEAT-TREATED ALLOY NO. 4 MATERIAL



[FIG. 9]

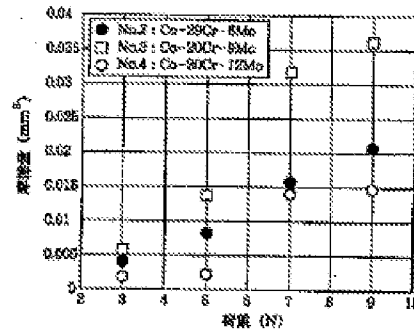
WEAR CHARACTERISTICS OF ALLOYS NO. 1 - 4



Key: y-axis) wear volume mm^3 ; x-axis) load (N)

[FIG. 10]

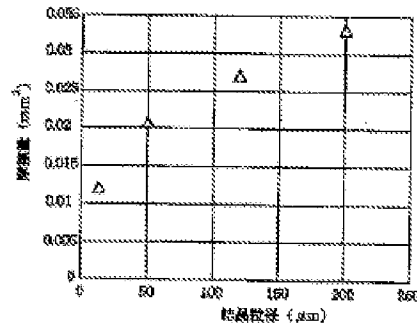
WEAR CHARACTERISTICS OF ALLOYS NO. 2 - 4



Key: y-axis) wear volume mm^3 ; x-axis) load (N)

[FIG. 11]

RELATIONSHIP BETWEEN WEAR VOLUME AND AVERAGE CRYSTAL-GRAIN SIZE IN FORGED ALLOY NO. 2 MATERIAL



Key: y-axis) wear volume mm^3 ; x-axis) crystal-grain size (μm)